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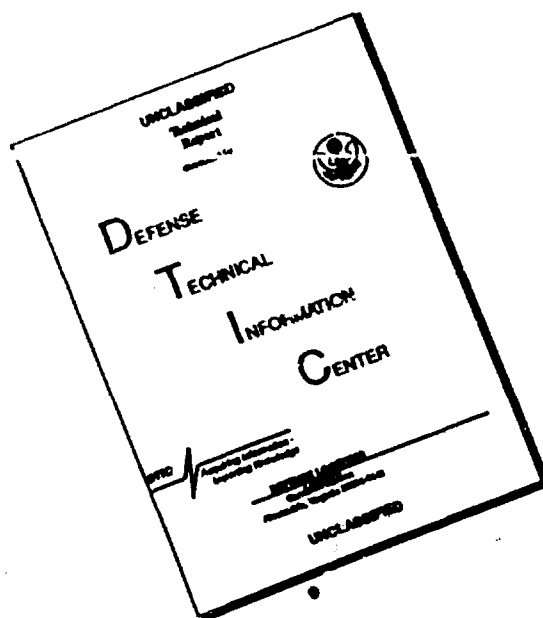
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13. ABSTRACT (Maximum 200 words) A goal of the research funded by this grant was to exploit the known photochemical and photophysical properties of (d ⁶) transition metal complexes for the preparation and utilization of novel microstructures in electroactive polymeric films. Thin polymeric films containing polypyridyl complexes of Fe ^{II} , Ru ^{II} , Os ^{II} , and Zn ^{II} have been prepared on a variety of conducting substrates by well established electropolymerization techniques. A majority of the research involved films prepared by the reductive polymerization of vinyl substituted pyridyl ligands, such as 4-vinyl-4-methyl-2,2'-bipyridine and 4-vinylpyridine.					
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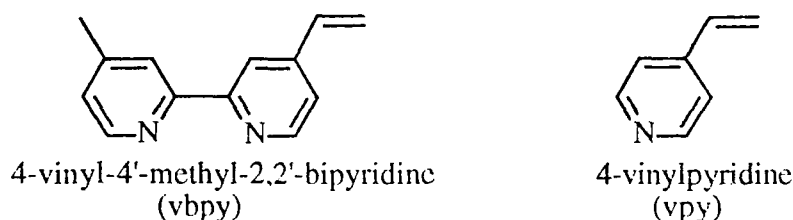
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Final Report
15 March 1990 - 14 March 1993

27664-CH-SM

The following report provides a summary of the major elements of the research funded by ARO grant #DAAL03-90-G-0062 during the period March 15, 1990 - March 14, 1993. Additional support of this work has been and continues to be provided by the supplementary ARO AASERT grant #DAAL03-92-G-0166.

One goal of the research funded by this grant was to exploit the known photochemical and photophysical properties of ($d\pi^6$) transition metal complexes for the preparation and utilization of novel microstructures in electroactive polymeric films. Thin polymeric films containing polypyridyl complexes of Fe^{II} , Ru^{II} , Os^{II} , and Zn^{II} have been prepared on a variety of conducting substrates by well established electropolymerization techniques. A majority of the research involved films prepared by the reductive polymerization of vinyl substituted pyridyl ligands, such as 4-vinyl-4'-methyl-2,2'-bipyridine (vbpy) and 4-vinylpyridine (vpy).



By repeatedly cycling the potential of the electrodes past the ligand reductions, polymeric films can be deposited in a controlled fashion as homopolymeric, copolymeric, and spatially segregated bilayer coatings.

A second major focus of the research performed involved the utilization and development of a wide range of analytical surface and microanalysis techniques; including X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), scanning tunneling and atomic force microscopies (STM/AFM), and secondary ion mass spectrometry (SIMS). In addition to providing information regarding the physical and chemical natures of the redox active polymeric films and microstructures, surface analytical studies were conducted for the development and critical evaluation of new analytical approaches for materials characterization.

Photophysical Studies

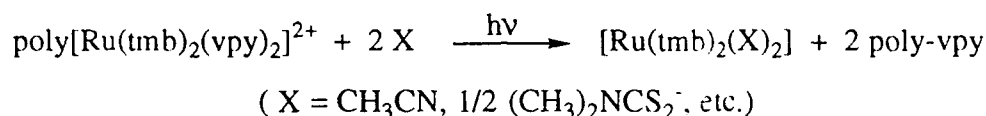
Photophysical measurements have been made on electropolymerized films of $\text{poly}[\text{Ru}(\text{vbpy})_3]^{2+}$ and $\text{poly}[\text{Os}(\text{vbpy})_3]^{2+}$ on optically transparent Sn doped In_2O_3 and compared to solution studies. The excited state lifetimes of these films exhibit dramatically shorter lifetimes than their monomeric solution analogues. One possible explanation for this is conduction band quenching of the chromophore's excited state by the semiconductor substrate. An alternative explanation is that self-quenching is occurring between neighboring sites in the polymer matrix. Photophysical studies conducted by using copolymeric films of $\text{poly}[\text{Ru}(\text{vbpy})_3]^{2+}/\text{poly}[\text{Zn}(\text{vbpy})_3]^{2+}$ exhibit a systematic increase in the luminescence efficiency and lifetimes as the ratio of zinc complexes in the film is increased. An explanation of the observed behavior is that the zinc sites act as "insulators" and reduce self-quenching of the ruthenium chromophores.

Electrochemiluminescence (ECL) has also been studied in thin polymeric films of $\text{poly}[\text{Ru}(\text{vbpy})_3]^{2+}$ and co- $\text{poly}[\text{Ru}(\text{vbpy})_3]^{2+}/[\text{Zn}(\text{vbpy})_3]^{2+}$ electropolymerized on platinum microband electrodes. ECL is observed due to self-annihilation reactions between Ru^{3+} and Ru^+ generated within the film by the application of a square wave potential (at ~ 100 to 500 Hz).

Microstructure Formation in Electropolymerized Films

The photophysical properties of ruthenium polypyridyl complexes have been used to create novel microstructures in polymeric films. In previous experiments we have shown that thin polymeric films of $\text{poly}[\text{Ru}(\text{tmb})_2(\text{vpy})_2]^{2+}$ (tmb is 4,4',5,5'-tetramethyl-2,2'-bipyridine) undergo

photochemical ligand loss as shown in the reaction below:



By using standard lithographic and masking techniques, it is possible to generate laterally resolved microstructures on electrode surfaces, with image resolution < 10 μm.

Ligand loss photochemistry in copolymerized films of poly[Ru(tmb)₂(vpy)₂]²⁺/poly[M(vbpy)₃]²⁺ (M = Ru or Os) on platinum electrodes results in loss of [Ru(tmb)₂]²⁺ fragments from the polymer matrix and the creation of molecular voids. The poly[Ru(vbpy)₃]²⁺/vpy films that remain were shown to act as size selective transport barriers toward diffusion to the inner electrode. Rotated disc and cyclic voltammetric experiments were conducted to assess the use of these structures for size-selective oxidation of a series of ferrocene derivatives. In other experiments, the vpy binding sites which are retained within the remaining poly[Os(vbpy)₃]²⁺ polymer matrix were then used to coordinate [Os(PMe₂Ph)₃Cl₂] following reduction of mer-Os(PMe₂Ph)₃Cl₃. By using masking techniques, it was possible to incorporate the Os^{III} complex with spatial control.

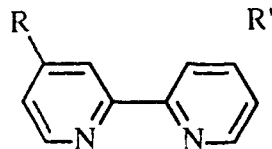
Polymeric films of poly[Ru(vbpy)₂(py)₂]²⁺ also undergo photochemical ligand substitution. Unlike their poly[Ru(bpy)₂(vpy)₂]²⁺ analogs, the crosslinking of the polymeric network is not diminished and the films remain intact. By utilizing established lithographic techniques, this chemistry has provided a basis for creating laterally resolved multicomponent assemblies. Two component arrays have been prepared by using Cl⁻, CN⁻, and (CH₃)₂NCS₂⁻ as the photosubstituted ligands. Cyclic voltammetry and small spot XPS analysis have been used to confirm the presence of two chemically different regions on the electrode surface. Film assemblies of this type may provide a basis for multicomponent, electrochromic displays.

Catalytic Oxidation of Benzyl Alcohol and Chloride Ion in poly[Ru(vbpy)₂(H₂O)₂]²⁺

Photolysis of poly[Ru(vbpy)₂(py)₂]²⁺ on glassy carbon electrodes in the presence of 0.1 M HClO₄ yields the substitution product, poly[Ru(vbpy)₂(H₂O)₂]²⁺, as characterized by cyclic voltammetry and UV-vis spectroscopy. The E_{1/2} for the Ru^{III/II} couple in these films has a pH dependence of ~60 mV/pH unit, as expected from analogous solution studies. These films have been shown to exhibit catalytic electrochemical behavior toward the oxidation of benzyl alcohol and Cl⁻. Lithographic and selective electropolymerization techniques (as described above) have been used to generate two dimensional arrays of the catalytic polymer on bare glassy carbon electrodes with lateral dimensions of ~350 μm.

Electropolymerization of Aldehyde- and Bromomethyl-Substituted Derivatives of 2,2'-Bipyridine

New chemical approaches to the formation of films by reductive electropolymerization were also pursued. They were based on polypyridyl complexes of Fe^{II}, Zn^{II}, and Ru^{II} containing aldehyde- and bromomethyl-substituted derivatives of 2,2'-bipyridine as shown below.



- | | |
|---|--|
| R = -CH ₃ , R' = -CHO | : 4-carboxaldehyde-4'-methyl-2,2'-bipyridine |
| R = -CH ₃ , R' = -CH ₂ Br | : 4-bromomethyl-4'-methyl-2,2'-bipyridine |
| R = R' = -CH ₂ Br | : 4-4'-bis(bromomethyl)-2,2'-bipyridine |

Upon electrochemical reduction, these complexes undergo polymerization via coupling reactions between electrochemically generated radicals of bromomethyl or carboxyaldehyde substituents. Polymeric films of poly[M^{II}(4-CHO-4'-CH₃-bpy)₃]²⁺ (M = Fe or Zn) were investigated by using attenuated total reflectance infrared spectroscopy (ATR-IR), fast atom bombardment mass spectrometry (FAB-MS), and ¹H NMR. The results were consistent with a polymerization mechanism involving a 1,2-diol link between bipyridine ligands. The linkage in polymeric films based on bromomethyl-substituted bipyridines is by C-C bond formation following reduction and Br⁻ loss. These films appear to be less dense and more permeable than films obtained by electrochemical polymerization of analogous complexes containing the vbpv ligand.

Angle Dependent X-ray Photoelectron Spectroscopy

Angle dependent X-ray photoelectron spectroscopy (ADXPS) was used to estimate the thickness of ultrathin polymeric films of co-poly[Ru(tmb)₂(vpy)₂]²⁺/poly[Os(vbpy)₃]²⁺ on platinum substrates, before and after photolysis. XPS overlay and Simplex based models were used to analyze the ADXPS data in order to quantify the depth profile concentration gradients of the samples. XPS data were collected by using a Perkin Elmer Physical Electronics Model 5400. There was good agreement in both the overlay and simplex calculated thicknesses to those predicted by electrochemical measurements on the unphotolyzed copolymeric film. Analysis of the photolyzed films suggested that thickness changes were minimal and consistent with the creation of molecular voids within the polymeric matrix. It was shown that ADXPS can be applied successfully to the routine analysis of electropolymerized films, provided accurate thickness measurements (from non-contact AFM) can be made on reference films for determination of parameters necessary for the XPS interpretation.

Three-Dimensional Imaging of Polymeric Arrays Based on Dynamic-SIMS

Image depth profiling with dynamic secondary ion mass spectrometry (SIMS) by using ion microscopy and digital imaging, provided high spatial resolution, 3-D images of patterned polymeric films prepared from [Ru(tmb)₂(vpy)₂]²⁺ and [Fe((BrCH₂)₂bpy)₃]²⁺. Although 3-D SIMS has been widely applied in semiconductor device characterization, this study represented a first attempt to characterize conductive polymeric arrays. The SIMS studies were useful in localizing the polymer domains, and the extent of polymer mixing within the microstructures. Volume-rendered images and reconstructed local area depth profiles indicated that electropolymerization of poly[Fe((BrCH₂)₂bpy)₃]²⁺ was not limited to the channels of the poly[Ru(tmb)₂(vpy)₂]²⁺ photoresist produced by lithographic techniques. Quantification of the SIMS image depth profiles required consideration of non-linearities of detection system, ion yield variations (especially transients at the film/substrate interface), and native and sputter-induced roughness in the polymeric films.

Scanned Probe Microscopies

Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been used to assess the surface structure (roughness and thickness) of electropolymerized polymeric films. Results of the scanned probe microscopies also provide insight into the effects of initial film surface roughness and chemical microhomogeneity on the sputter depth profiles obtained using secondary ion mass spectrometry (SIMS). Film structures have also been studied as a function of the monomeric conformation, i.e. *cis*- vs. *trans*- isomers of [Ru(bpy)₂(vpy)₂]²⁺. Conformation differences appear to affect the molecular density by varying the extent of crosslinking within the polymeric matrix.